Polymer Bulletin 2, 411–416 (1980)

Polymer Bulletin

Investigations on Organozinc Catalysts for the Maleic Anhydride-Propylene Oxide Copolymerization

W. Kuran and A. Niesłochowski

Institute of Organic Chemistry and Technology, Technical University (Politechnika),
00-662 Warsaw, ul.Koszykowa 75, Poland

Summary

The influence of Lewis acidity of homogeneous organozinc catalyst RZnEt (R=C_2H_5-, CH_3O-, CH_3COO-, 2-$CH_3OC_6H_4O$-, 3-$CH_3OC_6H_4O$- and $CH_3COCH=C(CH_3)O$-) on monomer distribution in maleic anhydride-propylene oxide copolymers produced by this catalyst has been investigated. It was found that increasing the acidity (electron-accepting properties) of the Zn atom in the catalyst molecule caused an increase in the number of propylene oxide units in the obtained copolymers and a decrease of their average molecular weight.

Introduction

Cyclic acid anhydrides were reported to form copolymers with cyclic ethers in the presence of anionic and cationic catalysts at high temperature (FISCHER 1960, SCHWENK et al. 1962, HABERMEIER et al.1967). Copolymers obtained by an anionic mechanism exhibited higher tendency towards alternation and higher molecular weigh $\overline{M}_n$ in comparison with those obtained by cationic mechanism (HILT et al.1967). Copolymerization of cyclic acid anhydrides with cyclic ethers in the presence of organometallic catalyst such as diethylzinc was postulated (INOUE et al.1969) to proceed via an anionic-coordination mechanism.

The authors have found recently (KURAN and NIESŁOCHOWSKI) that copolymers of nearly alternating structure can be obtained by copolymerization of maleic anhydride (MA) and propylene oxide (PO) using ethylzinc compounds ArOZnEt (Ar= 2,6-$(CH_3)_2C_6H_3$-, 2,6-$Cl_2C_6H_3$-, 2-$CH_3OC_6H_4$- and 2-$CH_3COC_6H_4$-) in donor solvents. It was proposed that complexation of the zinc atom in the catalyst molecule by a donor solvent or chelating ligand ArO- which results in the decrease of the electron-accepting properties of the Zn atom is the reason for the increase of the content of MA units in the

0170-0839/80/0002/0411/$01.20

MA-PO copolymers.

This paper presents the results of the quantitative examination of the dependence between electron-accepting properties of various ethylzinc catalysts (RZnEt; R=C_2H_5-, CH_3O-, CH_3COO-, 2-$CH_3OC_6H_4O$-, 3-$CH_3OC_6H_4O$- and $CH_3COCH=C(CH_3)O$-) and monomer distribution in resulting MA-PO copolymers. For this purpose the ^{1}H-NMR investigation of $Et_3N{\cdot}RZnEt$ complexes was applied. Triethylamine is a very suitable agent for examination of the electron-accepting properties of organometallic compounds (TAKASHI 1967, WESTERA et al. 1978). The results of the studies on the molecular weight distribution of MA-PO copolymers measured by GPC analysis are also presented.

Experimental

Materials

Diethylzinc was obtained according to the known method and purified by heating with sodium (NÜTZEL 1973). MA was distilled before use. PO was refluxed under nitrogen in the presence of lithium aluminium hydride and distilled before use. All other reactants and solvents were purified by standard methods and distilled in nitrogen atmosphere.

^{1}H-NMR measurements of RZnEt compounds and complexes $Et_3N{\cdot}RZnEt$

Catalysts (RZnEt) were prepared by introducing the compound with active hydrogen (HR) into a stirred solution of equimolar amount of $ZnEt_2$ in benzene (BOERSMA and NOLTES 1968). 1 Molar solutions of RZnEt compounds were used for spectroscopic measurements. ^{1}H-NMR spectra of RZnEt and complexes $Et_3N{\cdot}RZnEt$ were obtained with a JEOL JNM-MH-100 MHz spectrometer at temperature 30°C. The solvent served as a reference.

Copolymerization reactions

All polymerization reactions were carried out under nitrogen atmosphere in glass tubes provided with rubber stoppers afforded to introduce solutions by means of a syringe. 0.05 mole MA and 0.05 mole PO were introduced to 40 ml of toluene and the obtained mixture was shaken to give complete solution. 1 mmole of catalyst was then added as 1 Molar solution in toluene. Polymerizations were carried out at 80°C for 48 hrs. After completion of the reaction the content of the reaction vessel was dissolved in 50 ml CH_2Cl_2. The solution obtained was washed with 5% H_2SO_4, water and then dried. The solvents were evaporated from the solution and remaining oil after heating at 80°C under 0.5 mm Hg for a few hours was treated with CH_3OH. The part insoluble in CH_3OH (MA-PO copolymer) was analyzed by means ^1H-NMR spectroscopy according to described method (KERN and SCHAEFER 1967) and gel permeation chromatography. ^1H-NMR analyses were performed by Tesla B5487C spectrometer at 80 MHz at room temperature. Solutions of 10-15% copolymer in acetone-d_6 with a few percent of TMS standard were employed. GPC analyses were recorded in THF solution at 25°C by Waters Gel Permeation Chromatograph Modell 200. Molecular weights of the copolymers were measured by vapour pressure osmometer Hewlett-Packard 302B.

Results and Discussion

The results of the ^1H-NMR examination of RZnEt catalysts and their complexes with triethylamine are presented in Table 1. Electron-accepting properties of the Zn atom found for each catalyst are expressed by Zn electro-negativity calculated using the modified Dailey-Schoolery equation (NARASHIMA and ROGERS 1960). The difference in electro-negativity ΔX was taken as measure of the Lewis acidity (electron-accepting strength) of RZnEt catalyst. The catalysts presented in Table 1 are ordered according to their decreasing ΔX value, i.e. decreasing electron-accepting properties. Catalysts such as 3-$CH_3OC_6H_4OZnEt$, $CH_3COCH{=}C(CH_3)OZnEt$ and $CH_3COOZnEt$ are characterized by higher Lewis acidity than $ZnEt_2$, but CH_3OZnEt and 2-$CH_3OC_6H_4OZnEt$ have lower Lewis acidity than $ZnEt_2$. Considering the degree of alternation in MA-PO copolymers produced by RZnEt catalysts (Table 1) it is to be noticed that decreasing the electron-accepting properties of the catalyst results in the enhancement of the degree of the alternation in the copolymer.

The gel permeation chromatograms of the tetrahydrofuran solutions of the MA-PO copolymers produced by $ZnEt_2$, $CH_3COCH{=}C(CH_3)OZnEt$ and 3-$CH_3OC_6H_4OZnEt$ are shown in Figure 1. Determination of the average molecular weight $\overline{M}_n$ of the above copolymers is presented in Table 1. It is interesting to notice that using RZnEt catalysts in which electron-accepting properties decrease for MA-PO copolymerization results in formation of corresponding MA-PO copolymers characterized by lowered PO:MA unit ratio and enhanced average molecular weight $\overline{M}_n$ and polydispersity.

On the basis of the obtained results one can not judge about the mechanism of the MA-PO copolymerization by organozinc catalysts. It may be a simultaneous cationic and anionic-coordination mechanism resulting from different Lewis acidity of chain growth centers. Similarly an ionic mechanism was

TABLE 1

The influence of RZnEt catalyst Lewis acidity on the properties of maleic anhydride (MA) and propylene oxide (PO) copolymers produced by these catalysts.[a]

Catalyst RZnEt	Zn electro-negativity X[b]			Copolymer			
	RZnEt	RZnEt·Et_3N	ΔX	Yield %	Mole % of PO in alternating sequences[c]	PO:MA units[c]	$\bar{M}_n$[d]
3-$CH_3OC_6H_4OZnC_2H_5$	1.79	1.40	0.39	27	41	1.55	1250
$CH_3COCH{=}C(CH_3)OZnC_2H_5$	1.52	1.38	0.12	31	46	1.48	1430
$CH_3COOZnC_2H_5$[e]	1.49	1.42	0.07	47	48	1.47	1310
$C_2H_5ZnC_2H_5$[f]	1.45	1.39	0.06	60	49	1.44	1790
$CH_3OZnC_2H_5$[e]	1.52	1.51	0.01	62	52	1.42	1460
2-$CH_3OC_6H_4OZnC_2H_5$	1.60	1.59	0.01	40	53	1.40	1670

a) Copolymers obtained in toluene at 80°C.

b) Measured in benzene solution; $[RZnEt] = [Et_3N]$ = 1 mole/l; $X = 0.62\cdot\Delta_{CH_2\text{-}CH_3} + 2.07$

c) Obtained from triads concentrations in the methyl region of ^1H-NMR spectrum (KERN and SCHAEFER 1967).

d) Determined by vapor pressure osmometry in chloroform at 38°C.

e) Tetramer in benzene solution (INOUE et al. 1974).

f) Monomer in benzene solution (INOUE et al. 1974).

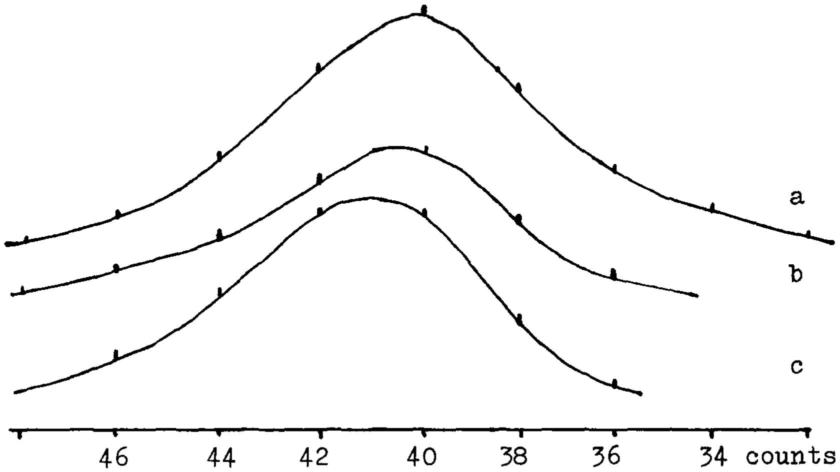

Figure 1. Molecular weight distribution of copolymers measured by gel permeation chromatography as produced by the catalysts a) $ZnEt_2$ $\overline{M}_w/\overline{M}_n = 3.46$, b) $CH_3COCH{=}C(CH_3)OZnEt$ $\overline{M}_w/\overline{M}_n = 1.99$ and c) 3-$CH_3OC_6H_4OZnEt$ $\overline{M}_w/\overline{M}_n = 1.82$. GPC calibration was based on polystyrene.

postulated earlier for PO homopolymerization by $ZnEt_2/H_2O$ system (ISCHIMORI et al. 1968). Catalysts of relatively strong electron-accepting properties producing a low-molecular-weight MA-PO copolymer fraction seem to react mainly as cationic initiators. On the other hand catalysts of lower Lewis acidity which produce a relatively high-molecular-weight copolymer fraction probably promote mainly MA-PO copolymerization by an anionic-coordination machanism (HILT et al. 1967).

As far as the synthesis of completly alternating copolymers of MA and PO is concerned, in the light of the present paper it is apparent that this purpose may be achieved by applying organometallic catalysts with low Lewis acidity of metallic center.

Acknowledgements

The authors wish to thank Prof. J. Brzeziński from Institute of Industrial Chemistry - Warsaw for GPC analysis.

References

BOERSMA, J. and NOLTES, J.G.: Organozinc Coordination Chemistry, The Netherlands; International Lead Zinc Research

Organization, Inc. (1968)
FISCHER, R.F.: J.Polym.Sci. 44, 155 (1960)
HABERMEIER, J., REICHERT, K.H. and HAMANN, K.: J.Polym.Sci.C 16, 2131 (1967)
HILT, A., REICHERT, K.H. and HAMANN, K.: Makromol. Chem. 101, 246 (1967)
INOUE, S., KITAMURA, K. and TSURUTA, T.: Makromol. Chem. 126, 250 (1969)
INOUE, S., KOBAYASHI, M. and TOZUKA, T.: J.Org.Chem. 81, 17 (1974)
ISHIMORI, M., NAKASUGI, O., TAKEDA, N. and TSURUTA, T.: Makromol.Chem. 115, 103 (1968)
KERN, R.J. and SCHAEFER, J.: J.Am.Chem.Soc. 89, 6 (1967)
KURAN, W. and NIESŁOCHOWSKI, A.: will be published
NARASHIMA, P.T. and ROGERS, M.T.: J.Am.Chem.Soc. 82, 5983 (1960)
NUTZEL, K.: Methoden der organischen Chemie Vol. 13/2a, 584, Stuttgart; G.Thieme Verlag, (1973)
SCHWENK, E., GULBINS, K., ROTH, M., BENZING, G., MAYSENHOLDER, R. and HAMANN, K.: Makromol.Chem. 51, 53 (1962)
TAKASHI, Y.: Bull.Chem.Soc.Japan 40, 1001 (1967)
WESTERA, G., BLOMBERG, C. and BICKELHAUPT, F.: J.Organomet.Chem. 155, C 55 (1978)

Received February 6/ March 9, 1980
Accepted March 14, 1980